

Cite this as:A. Karton. *Journal of Physical Chemistry A*, 126, 8544–8555 (2022).

DOI: 10.1021/acs.jpca.2c06522

Tightening the screws: The importance of tight d functions in coupled-cluster calculations up to the CCSDT(Q) level

Amir Karton*

School of Science and Technology, University of New England, Armidale, NSW 2351, Australia.

ABSTRACT: It is well established that the basis set convergence of the correlation consistent (cc-pVnZ) basis sets depends on the presence of high-exponent ‘tight’ d functions in the basis set for second-row atoms. The effect has been linked to low-lying $3d$ virtual orbitals approaching the valence shell. However, since most of this effect is captured at the SCF level, the effect of tight d functions in high-level coupled-cluster calculations has not been extensively studied. Here, we construct an extensive dataset of 45 second-row species to examine the effect of tight d functions in CCSD, CCSD(T), CCSDT, and CCSDT(Q) calculations in conjunction with basis sets of up to sextuple- ζ quality. The selected set of molecules covers the gamut from systems where the tight d functions play a relatively minor role (e.g., SiH, SH, SiF, PF₃, HOCl, Cl₂, and C₂Cl₂) to challenging systems containing a central second-row atom bonded to many oxygen or fluorine atoms (e.g., PF₅, SF₆, SO₃, ClO₃, and HClO₄) and systems containing many second-row atoms (e.g., P₄, S₄, CCl₄, and C₂Cl₆). In conjunction with the cc-pVDZ basis set, we find chemically significant contributions to the total atomization energies (TAEs) of up to ~ 2 kcal/mol at the CCSD level, ~ 1 kcal/mol at the (T) level, and contributions of up to ~ 0.1 kcal/mol for the post-CCSD(T) components. The effects of the tight d functions are diminished with the size of the basis set; however, they are still chemically significant at the CCSD and (T) levels. For example, with the cc-pVTZ basis set, we obtain contributions to the TAEs of up to ~ 1.5 and ~ 0.3 kcal/mol at the CCSD and (T) levels, respectively; and with the cc-pVQZ basis set, we obtain contributions of up to ~ 1.0 and ~ 0.2 kcal/mol at the CCSD and (T) levels, respectively. We also find that a simple natural bond orbital (NBO) population analysis of the $3d$ orbitals of the second-row atom provides a useful *a priori* indicator of the magnitude of the effect of tight d functions on post-CCSD(T) contribution to the TAEs in oxide and fluoride systems. These results are particularly important in the context of high-level composite ab initio methods capable of confident benchmark accuracy in thermochemical predictions.

Keywords: CCSD • CCSD(T) • CCSDT • CCSDT(Q) • correlation-consistent basis sets • composite ab initio methods

*E-Mail: amir.karton@une.edu.au

1. Introduction

The correlation consistent basis sets are designed specifically for correlated ab initio calculations. They represent relatively compact basis sets for recovering the correlation energy. An important property of these basis sets is that they treat radial and angular correlation in a balanced way, and the completeness of the angular and radial parts is systematically improved with the highest cardinal number n present in the basis set (cc-pVnZ).^{1,2,3,4} Thus, the cc-pVnZ ($n = D, T, Q, 5, 6$) basis set sequence provides energies (as well as other properties) that systematically converge to the complete basis set (CBS) limit. Thus, the correlation consistent basis sets are ideal for basis set extrapolations,^{5,6,7,8,9} and are heavily utilized in composite ab initio procedures.^{10,11,12,13,14,15,16,17,18,19,20,21,22} For example, the Weizmann- n family of methods use the following two-point extrapolation formula for the correlation components:^{11,16,19,23,24,25,26,27}

$$E_{L_{max}}^{corr} = E_{\infty}^{corr} + AL_{max}^{-\alpha}$$

where E^{corr} denotes the contribution to the correlation energy, for example, coupled cluster with singles and doubles (CCSD), quasiperturbative connected triple excitations ((T)), and post-CCSD(T) correlation contributions, and α is the decay exponent with an asymptotically limiting L_{max}^{-3} convergence behavior for the correlation energy.^{8,23,24,25,26,27,28,29}

Several years after the development of the correlation consistent basis sets, a deficiency was noted for second-row elements, namely, that the convergence of the cc-pVnZ series strongly depends on the presence of extra high-exponent (or ‘tight’) d functions in the basis set due to inner polarization effects.^{11,30,31,32,33,34,35} It was also found that this deficiency is exacerbated in pseudohypervalent systems involving a central second-row atom in a high formal oxidation state.^{36,37,38} An extreme example is Cl_2O_7 in which the addition of a single d function to the cc-pVDZ basis set has an effect on the order of $100 \text{ kcal mol}^{-1}$ on the self-consistent field (SCF) binding energy.³⁶ The effect is rooted in the low-lying $3d$ virtual

orbitals approaching the valence shell and thus becoming better acceptors for back-donation from the oxygens lone pairs. This shortcoming was remedied by the addition of high-exponent d functions for second-row atoms in the cc-pV($n+d$)Z basis sets.³ In these improved basis sets, a high-exponent d function was added to the cc-pV n Z basis sets, and the other d functions were reoptimized. The extra d function can be viewed as a polarization function for the inner part of the valence orbitals, which are ‘tighter’ than the polarization functions for the outer part of the valence orbitals.

The cc-pV($n+d$)Z basis sets have become the de facto standard in ab initio calculations involving second-row atoms, and their effects on the energetic properties of second-row systems have been examined in several studies.^{3,36,37,38,39,40,41,42,43,44,45,46} However, these studies mostly focused on the effect of tight d functions in SCF and density functional theory (DFT) calculations. The studies focusing on the correlation components in CCSD and CCSD(T) calculations were limited to a fairly small set of molecules such as CS, CS₂, SO, SO₂, SOH, and HSO.^{3,39,40,41,42} It is therefore of interest to examine the effects of tight d functions in CCSD and CCSD(T) correlation energies across a broad and diverse set of second-row molecules. Furthermore, it is important to examine the effects of tight d functions on post-CCSD(T) correlation contributions. The latter point is particularly relevant in the context of high-level composite ab initio methods since an effective strategy for reducing the steep computational cost of the valence post-CCSD(T) calculations (e.g., CCSDT, CCSDT(Q), etc.) is to omit the tight d functions. This strategy is adopted, for example, in the Weizmann-4 (W4) composite ab initio method, which approximates the CCSDTQ5/CBS energy (i.e., the coupled-cluster energy with up to quintuple excitations at the infinite basis-set limit) uses the following basis sets (or basis set extrapolations) in the valence correlation calculations: jul-cc-pV{5,6}Z+d (CCSD), jul-cc-pV{Q,5}Z+d (CCSD(T)), cc-pV{D,T}Z (CCSDT), cc-pVTZ (CCSDT(Q)), cc-pVDZ (CCSDTQ), and cc-pVDZ(sp) (CCSDTQ5)

(where the prefix ‘jul’ indicates the omission of diffuse functions from hydrogen,⁴⁷ and VDZ(sp) is a truncated version of the cc-pVDZ basis set).²⁵ Since theories like W4 are designed to provide confident sub-kJ mol⁻¹ accuracy, it is of interest to see if the omission of tight *d* functions in the post-CCSD(T) calculations can affect thermochemical properties at the sub-kJ mol⁻¹ level.

In the present work, we investigate the effect of tight *d* functions on the total atomization energies of a large and diverse set of 45-second-row molecules with up to eight non-hydrogen atoms. We consider the cc-pVnZ (*n* = D–6) basis sets as well as the cc-pV{D,T}Z and cc-pV{T,Q}Z basis set extrapolations. We note that these basis set extrapolations are used, respectively, for calculating the Δ CCSD and Δ (T) components in W1 theory, whereas the cc-pV{D,T}Z basis set extrapolation is used for calculating the Δ T–(T) component in W3 and W4 theories.^{16,19,22} Importantly, the considered set includes a statistically meaningful representation of a broad spectrum of bonding situations and electronic structures. Namely, it includes:

- Nine hydrides (e.g., AlH, AlH₃, SiH, SiH₄, Si₂H₆, PH₃, HS, H₂S, HCl)
- Ten fluorides (e.g., AlF, AlF₃, SiF, SiF₄, PF₃, PF₅, SF₆, ClF, ClF₃, ClF₅)
- Ten oxides (e.g., SO, SO₂, SO₃, HOCl, HOClO, HOClO₂, HClO₄, ClO, OClO, ClO₃)
- Eight pure second-row systems (e.g., AlCl, AlCl₃, P₂, P₄, S₂, S₃, S₄, Cl₂)
- Eight organic systems (e.g., CS, CS₂, CF₂Cl₂, CCl₂, CCl₄, C₂Cl₂, C₂Cl₄, C₂Cl₆)

We examine the effect of adding tight *d* functions on the post-SCF contributions to total atomization energies. We consider the following correlation components in conjunction with the cc-pVnZ and cc-pV(*n*+*d*)Z basis sets (*n* = D, T, Q, 5, 6):

- Connected doubles, CCSD–SCF, Δ CCSD
- Noniterative connected triples, CCSD(T)–CCSD, Δ (T)
- Full-iterative connected triples, CCSDT–CCSD(T), Δ T–(T)

- Noniterative connected quadruples, CCSDT(Q)–CCSDT, $\Delta(Q)$

2. Computational Methods

All CCSD(T)/cc-pV(Q+d)Z optimized geometries are taken from the W4-17 database.⁴⁸ We note that geometries optimized at this level of theory are in close agreement with CCSD(T)/cc-pV(6+d)Z geometries, with a mean absolute deviation (MAD) of merely 0.001 Å over a wide range of organic and inorganic molecules.⁴⁹ All energy calculations were carried out using the MRCC program suite^{50,51} with the regular cc-pVnZ and cc-pV(n+d)Z correlation-consistent basis sets ($n = D, T, Q, 5, 6$). For brevity, these basis sets are denoted by VnZ and V(n+d)Z, respectively, throughout this article. All basis set extrapolations employ the $E(L) = E_\infty + A/L^\alpha$ two-point extrapolation formula with $\alpha = 3$ (where L is the highest angular momentum represented in the basis sets for the non-hydrogen atoms). Basis set extrapolations using the VnZ and V(n+1)Z basis sets are denoted by V{n,n+1}Z. All calculations are nonrelativistic and are carried out within the frozen-core approximation, i.e., the 1s orbitals for first-row atoms and the 1s, 2s, and 2p orbitals for second-row atoms are constrained to be doubly occupied in all configurations. For open-shell systems, the unrestricted Hartree–Fock formalism is employed. Natural bond orbital (NBO) population analyses are carried out using the Gaussian 16 program suite.^{52,53}

3. Results and Discussion

3.1. Overview of second-row species considered in the present work. We consider a large and diverse set of 45 second-row molecules with up to eight non-hydrogen atoms. This dataset includes 20 chlorine, 11 sulfur, 5 phosphorous, 5 silicon, and 6 aluminum compounds. Table 1 gives an overview of the considered species (the complete list of molecules is given in Table 2). The considered set consists of 9 hydrides, 10 fluorides, 10 oxides, 8 pure second-row, and 8 organic systems. Thirty seven of the systems are closed-

shell, and 8 are open-shell species (6 radicals and 2 triplet systems). In addition, the species in the set span the gamut from systems dominated by mild (e.g., SiH₄, PH₃, HOCl) to moderate nondynamical correlation (e.g., S₃, S₄, OClO). Importantly, the chosen set also spans the gamut from systems with a central second-row atom in a low (e.g., AlH₃, SiH₄, H₂S), medium (e.g., PF₃, ClF₃, HOClO), and high (e.g., SO₃, SF₆, HClO₄) formal oxidation state.

Table 1. Overview of the second-row species considered in the present work.

	Number of species
Hydrides	9 ^a
Fluorides	10 ^a
Oxides	10 ^a
Pure second-row	8 ^a
Organic	8 ^a
Closed-shell species	37
Open-shell species	8 ^b
Second-row atom in formal oxidation state +1, +2	30
Second-row atom in formal oxidation state +3	5 ^c
Second-row atom in formal oxidation state +4	3 ^d
Second-row atom in formal oxidation state +5	3 ^e
Second-row atom in formal oxidation state +6	3 ^f
Second-row atom in formal oxidation state +7	1 ^g

^aFor the list of molecules see Table 2. ^bThe open-shell systems are SiH, SH, SiF, SO, S₂, ClO, OClO, and ClO₃. ^cAlF₃, AlCl₃, PF₃, HOClO, ClF₃. ^dSiF₄, SO₂, ClO₂. ^ePF₅, HOClO₂, ClF₅. ^fSO₃, SF₆, ClO₃. ^gHClO₄.

3.2 Effect of d functions on connected double excitations. Table 2 gives the differences between the CCSD correlation component of the total atomization energy (TAE) calculated with the VnZ and $V(n+d)Z$ basis sets ($n = D-6$). The tabulated values are color coded with colors ranging from dark red (large positive values) to yellow (small values) to dark green (large negative values). Let us start by making the following general observations regarding the effect of tight d functions on the Δ CCSD component of the TAEs. Since both the VnZ and $V(n+d)Z$ basis sets converge to the same infinite basis set limit, the effect of the tight d functions diminishes with the highest angular momentum present in the basis set (D, T, Q, 5, 6). For example, the RMS difference over the entire set of 45 molecules is 0.69 (VDZ), 0.41

(VTZ), and 0.24 (VQZ) kcal mol⁻¹. The systems for which we were able to obtain results using larger basis sets are not sufficiently representative; however, we note that this trend continues to persist for the V5Z and V6Z basis sets for the systems for which we have these results. We also note that, the addition of tight *d* functions tends to systematically increase the Δ CCSD component of the TAEs for the fluorides and oxides but systematically decreases the Δ CCSD component of the hydrides, pure second-row, and organic systems.

Table 2. Differences between the Δ CCSD component of the total atomization energy (TAE) obtained with VnZ and $V(n+d)Z$ basis sets ($TAE(VnZ) - TAE(V(n+d)Z)$ in kcal mol⁻¹) for a set of 45 second-row systems. Heatmapping is from red (largest positive values) to yellow (small values) to green (largest negative values). Effect of tight d functions on the Δ CCSD component of the total atomization energies (TAEs) of 45 second-row systems.^a

		VDZ	VTZ	VQZ	V5Z	V6Z	V{D,T}Z	V{T,Q}Z
Hydrides	AlH	0.014	0.018	0.011	0.000	0.000	0.019	0.006
	AlH ₃	0.260	0.083	0.039	0.008	0.002	0.009	0.006
	SiH	0.172	0.073	0.029	0.001	0.000	0.031	-0.003
	SiH ₄	0.721	0.262	0.100	0.030	0.012	0.068	-0.018
	Si ₂ H ₆	1.347	0.472	0.171	0.050		0.104	-0.049
	PH ₃	0.658	0.272	0.088	0.008	0.001	0.109	-0.045
	HS	0.247	0.111	0.037	-0.007	-0.002	0.053	-0.017
	H ₂ S	0.397	0.176	0.055	-0.005	-0.002	0.083	-0.033
	HCl	0.161	0.065	0.018	-0.009	-0.001	0.025	-0.017
Fluorides	AlF	-0.230	-0.055	-0.038	-0.019	-0.006	0.018	-0.025
	AlF ₃	-0.478	-0.178	-0.119	-0.053		-0.051	-0.076
	SiF	0.053	-0.016	-0.032	-0.014	0.005	-0.045	-0.044
	SiF ₄	-0.475	-0.408	-0.294	-0.055		-0.380	-0.210
	PF ₃	-0.043	-0.196	-0.211	-0.048		-0.260	-0.223
	PF ₅	-0.461	-0.508	-0.423			-0.528	-0.361
	SF ₆	-0.641	-0.634	-0.431			-0.630	-0.283
	ClF	0.030	0.035	0.009	0.008	0.003	0.037	-0.011
	ClF ₃	0.010	-0.043	-0.049	0.011		-0.065	-0.054
Oxides	ClF ₅	0.223	-0.077	-0.037			-0.203	-0.009
	SO	0.426	0.167	0.063	0.022	0.010	0.058	-0.013
	SO ₂	0.176	-0.098	-0.133	-0.013		-0.214	-0.159
	SO ₃	-0.294	-0.440	-0.372	-0.054		-0.501	-0.322
	HOCl	0.086	0.051	0.015	0.008		0.036	-0.010
	HOClO	-0.398	-0.247	-0.175	-0.015		-0.184	-0.122
	HOClO ₂	-1.100	-0.760	-0.493			-0.617	-0.298
	HClO ₄	-2.187	-1.523	-0.948			-1.243	-0.529
	ClO	-0.109	-0.109	-0.082	-0.019	-0.005	-0.109	-0.063
Pure second-row	OCIO	-0.659	-0.407	-0.280	-0.032		-0.300	-0.187
	ClO ₃	-1.674	-1.096	-0.699			-0.853	-0.410
	AlCl	0.041	0.012	-0.031	-0.001	0.001	0.000	-0.063
	AlCl ₃	0.128	0.082	-0.091	0.028		0.062	-0.217
	P ₂	0.793	0.362	0.098	-0.023	-0.008	0.180	-0.095
	P ₄	1.721	0.633	0.118	-0.018		0.175	-0.258
	S ₂	0.591	0.275	0.124	0.028	0.009	0.142	0.014
	S ₃	0.751	0.246	0.053	-0.004		0.034	-0.087
	S ₄	1.156	0.385	0.112			0.060	-0.086
Organic	Cl ₂	0.085	0.079	0.001	0.005	0.001	0.076	-0.055
	CS	0.449	0.230	0.101	0.022	0.010	0.138	0.006
	CS ₂	0.655	0.270	0.107	0.021		0.108	-0.012
	CF ₂ Cl ₂	0.257	0.212	0.084	0.056		0.193	-0.009
	CCl ₂	0.218	0.153	0.058	0.044		0.125	-0.012
	CCl ₄	0.498	0.398	0.156	0.121		0.356	-0.021
	C ₂ Cl ₂	0.188	0.172	0.068	0.036		0.165	-0.009
	C ₂ Cl ₄	0.454	0.372	0.142			0.337	-0.025
	C ₂ Cl ₆	0.672	0.583	0.234			0.545	-0.021
Overall stat.^b	RMSD	0.692	0.411	0.244			0.327	0.162
	MAD	0.497	0.290	0.156			0.212	0.102
	MSD	0.109	-0.012	-0.063			-0.063	-0.101

^aSome calculations for the larger systems proved beyond our available computational resources. ^bStatistics are taken over the above 45 differences for basis sets for which we have results for all systems. RMSD = Root-mean-square difference, MAD = mean absolute difference, MSD = mean signed difference.

As expected, the effect of the *d* functions is chemically significant in conjunction with the small VDZ basis set. For 21 out of the 45 second-row systems (i.e., ~50% of systems), the *d* functions affect the TAEs by amounts equal to or larger than 0.5 kcal mol⁻¹. Most notably, the addition of *d* functions increases the TAEs of the chlorine oxides HOClO₂, ClO₃, and HClO₄ by 1.10–2.19 kcal mol⁻¹. Large effects are also seen for S₄ and P₄, where the *d* functions reduce the TAEs by 1.16 and 1.72 kcal mol⁻¹, respectively. However, somewhat unexpectedly, relatively large effects are observed for several hydrides, which are neither pseudohypervalent nor include many second-row atoms. Inspection of the hydrides in Table 2 reveals that the inclusion of tight *d* functions affects the TAEs by as much as 0.66 (PH₃), 0.72 (SiH₄), and 1.35 (Si₂H₆) kcal mol⁻¹. It is important to note that the large effects obtained for SiH₄ and Si₂H₆ are due almost entirely to the effect of the *d* functions on the Si atom. Namely, the addition of the *d* functions affects the absolute Δ CCSD component by 0.70 (Si), -0.02 (SiH₄), and 0.05 (Si₂H₆) kcal mol⁻¹. This is true to a lesser extent for PH₃, where the addition of the *d* functions affects the absolute Δ CCSD component by 1.19 (Si) and 0.53 (PH₃) kcal mol⁻¹. For both SiH₄ and PH₃, the effect of the *d* functions is reduced to 0.3 kcal mol⁻¹ with the VTZ basis set and to 0.1 kcal mol⁻¹ with the VQZ basis set.

In conjunction with the VTZ basis set, the effect of the tight *d* functions exceed 1 kcal mol⁻¹ for two chlorine oxides, namely, -1.10 (ClO₃) and -1.52 (HClO₄) kcal mol⁻¹. Three other pseudohypervalent systems for which the addition of *d* functions affects the TAEs by over 0.5 kcal mol⁻¹ are HOClO₂, SF₆, and PF₅, where the addition of the *d* functions increases the TAEs by 0.76, 0.63, and 0.51 kcal mol⁻¹, respectively. Large effects exceeding 0.5 kcal mol⁻¹ are also obtained for systems that are clearly not pseudohypervalent but in turn include a large number of second-row atoms. Namely, C₂Cl₆ and P₄, where the addition of the *d* functions reduces the TAEs by 0.58 and 0.63 kcal mol⁻¹, respectively. Finally, we note that even with the relatively large VQZ basis set, the effect of the tight *d* functions can be quite

significant, reaching up to -0.70 and -0.95 kcal mol⁻¹ for ClO₃ and HClO₄, respectively (Table 2).

A word is due on the difference between basis set incompleteness and the inability of a basis set to cope with pseudohypervalent systems. The above results show that the addition of tight *d* functions on second-row atoms has a pronounced effect for both pseudo-hypervalent systems (e.g., HClO₄) and systems containing multiple second-row atoms (e.g., P₄ and S₄). To gain a better understanding of the magnitude of these conflating effects, it is instructive to examine the effect of adding tight *d* functions for a series of molecules, all containing the same central second-row atom, but with an increasing formal oxidation state. Here, we consider the HOCl, HOClO, HOClO₂, HClO₄ series. For example, for the VDZ basis set, the addition of the tight *d* functions affects the TAEs by 0.09 (HOCl), -0.40 (HOClO), -1.10 (HOClO₂), and -2.19 (HClO₄) kcal mol⁻¹ (Table 2). In all cases, the same number of basis functions are added in the V(D+d)Z calculation; however, the pseudohypervalent character and the number of polar bonds increase along the series. Thus, the increased effect of the tight *d* functions along this series may be attributed to these electronic effects. Similar trends are observed for the VTZ and VQZ basis sets.

3.3 Perturbative, noniterative connected triple excitations. Table 3 lists the differences between the $\Delta(T)$ component of the TAE calculated with the VnZ and $V(n+d)Z$ basis sets ($n = D-6$). With the main exception of some hydrides, the addition of tight d functions increases the magnitude of the $\Delta(T)$ contribution to the TAEs. This contrasts with the ΔCCSD correlation contribution, where the addition of the d functions does not tend to systematically increase the TAEs across all systems (*vide supra*). Let us start by examining the results for the VDZ basis set. The largest effects are seen for systems containing multiple second-row atoms. For example, upon addition of the d functions the $\Delta(T)$ contribution to the TAE increases by 0.73 (S_4), 0.62 (C_2Cl_6), 0.47 (S_3), 0.42 (C_2Cl_4), 0.39 (CCl_4), and 0.38 (P_4) kcal mol⁻¹. As expected, chemically significant effects are also observed for the chlorine oxides, namely 0.49 (ClO_3), 0.48 ($HClO_4$), 0.38 ($HOClO_2$), 0.36 ($OCIO$), and 0.25 ($HOClO$) kcal mol⁻¹. As is the case for the ΔCCSD component, the effect for the sulfur oxides is significantly diminished relative to the chlorine oxides and does not exceed 0.1 kcal mol⁻¹. Likewise, the effects for the fluorine oxides are relatively minor, with the largest effects of 0.10 (PF_5), 0.13 (ClF_3), and 0.15 (SF_6) kcal mol⁻¹.

Table 3. Differences between the $\Delta(T)$ component of the total atomization energy (TAE) obtained with VnZ and $V(n+d)Z$ basis sets ($TAE(VnZ)-TAE(V(n+d)Z)$ in kcal mol⁻¹) for a set of 45 second-row systems. Heatmapping is from red (largest positive values) to yellow (small values) to green (largest negative values).^a

		VDZ	VTZ	VQZ	V5Z	V6Z	V{D,T}Z	V{T,Q}Z
Hydrides	AlH	0.005	0.002	0.002	0.001	0.000	0.001	0.002
	AlH ₃	0.017	0.008	0.006	0.002	0.001	0.004	0.005
	SiH	0.005	0.008	0.005	0.001	0.001	0.009	0.003
	SiH ₄	0.038	0.034	0.020	0.006	0.003	0.032	0.009
	Si ₂ H ₆	0.047	0.060	0.032	0.010		0.066	0.012
	PH ₃	0.002	0.033	0.017	0.002	0.002	0.046	0.005
	HS	-0.022	0.004	0.002	-0.003	-0.001	0.015	0.001
	H ₂ S	-0.043	0.007	0.004	-0.004	-0.001	0.028	0.002
	HCl	-0.051	-0.010	-0.005	-0.006	-0.002	0.006	-0.001
Fluorides	AlF	0.015	0.001	-0.001	-0.002	0.000	-0.005	-0.002
	AlF ₃	0.011	-0.017	-0.014	-0.007		-0.029	-0.012
	SiF	0.010	0.004	0.001	0.000	0.001	0.002	-0.002
	SiF ₄	-0.047	-0.056	-0.038	-0.008		-0.059	-0.025
	PF ₃	-0.054	-0.027	-0.020	-0.003		-0.015	-0.015
	PF ₅	-0.103	-0.069	-0.049			-0.055	-0.035
	SF ₆	-0.153	-0.080	-0.065			-0.049	-0.055
	ClF	-0.085	-0.031	-0.016	-0.004	-0.001	-0.008	-0.005
	ClF ₃	-0.126	-0.046	-0.025	-0.006		-0.012	-0.010
Oxides	ClF ₅	-0.067	0.014	0.014			0.048	0.013
	SO	-0.095	-0.011	-0.006	-0.002	-0.001	0.024	-0.002
	SO ₂	0.027	0.047	0.025	0.005		0.056	0.008
	SO ₃	-0.069	-0.019	-0.020	-0.007		0.003	-0.021
	HOCl	-0.098	-0.034	-0.019	-0.006		-0.007	-0.008
	HOClO	-0.246	-0.113	-0.071	-0.015		-0.056	-0.041
	HOClO ₂	-0.384	-0.182	-0.113			-0.097	-0.063
	HClO ₄	-0.480	-0.281	-0.176			-0.198	-0.099
	ClO	-0.146	-0.067	-0.042	-0.013	-0.005	-0.034	-0.023
Pure second-row	OCIO	-0.356	-0.152	-0.095	-0.019		-0.066	-0.053
	ClO ₃	-0.493	-0.250	-0.156			-0.148	-0.087
	AlCl	-0.103	-0.031	-0.015	-0.003	-0.001	-0.001	-0.004
	AlCl ₃	-0.298	-0.089	-0.045	0.002		-0.002	-0.012
	P ₂	-0.184	-0.003	-0.004	-0.007	-0.002	0.073	-0.005
	P ₄	-0.385	-0.051	-0.049	-0.015		0.089	-0.047
	S ₂	-0.254	-0.059	-0.032	-0.014	-0.006	0.023	-0.012
	S ₃	-0.473	-0.118	-0.066	-0.025		0.031	-0.029
	S ₄	-0.730	-0.201	-0.112			0.021	-0.046
Organic	Cl ₂	-0.190	-0.070	-0.040	-0.016	-0.006	-0.019	-0.018
	CS	-0.150	-0.024	-0.007	-0.001	-0.001	0.029	0.005
	CS ₂	-0.321	-0.087	-0.041	-0.012		0.011	-0.007
	CF ₂ Cl ₂	-0.181	-0.047	-0.023	0.002		0.009	-0.006
	CCl ₂	-0.252	-0.080	-0.043	-0.007		-0.008	-0.015
	CCl ₄	-0.389	-0.110	-0.058	-0.002		0.008	-0.020
	C ₂ Cl ₂	-0.211	-0.071	-0.038	-0.001		-0.012	-0.014
	C ₂ Cl ₄	-0.419	-0.133	-0.072			-0.012	-0.028
	C ₂ Cl ₆	-0.617	-0.187	-0.097			-0.006	-0.032
Overall stat.^a	RMSD	0.260	0.095	0.057			0.052	0.030
	MAD	0.188	0.067	0.040			0.034	0.020
	MSD	-0.180	-0.057	-0.034			-0.006	-0.017

^aFootnotes *a* and *b* to Table 2 apply here.

The effect of the tight d functions on the $\Delta(T)$ component diminishes significantly for the VTZ basis set relative to the VDZ basis set. In most cases, the magnitude of the effect is reduced by 50–80%. Apart from chlorine oxides and molecules containing many second-row atoms, the addition of the d functions affects the $\Delta(T)$ component by less than 0.1 kcal mol⁻¹. For all the chlorine oxides with multiple oxygen atoms, the effect of the d functions is rather large, ranging from 0.25 (HOClO) to 0.49/0.48 (ClO₃/HClO₄) kcal mol⁻¹. The largest effects for the systems containing many second-row atoms are obtained for S₄ (0.20) and C₂Cl₆ (0.19 kcal mol⁻¹). For the VQZ basis set, the effect of the d functions is still pronounced for chlorine oxides and molecules containing many second-row atoms. For example, the $\Delta(T)$ component of the TAE is increased by over 0.1 kcal mol⁻¹ for HOClO₂ (0.11), S₄ (0.11), ClO₃ (0.16), and HClO₄ (0.18 kcal mol⁻¹). For the systems for which we have results with the V5Z and V6Z basis sets, the effects of the tight d functions are chemically insignificant.

Despite the large effects of the tight d functions on the VDZ basis set, the V{D,T}Z basis set extrapolation is affected by less than 0.1 kcal mol⁻¹ in most cases. The exceptions to this are the chlorine oxides, where the $\Delta(T)$ component of the TAE is affected by as much as -0.20 (HClO₄), -0.15 (ClO₃), and -0.10 (HOClO₂) kcal mol⁻¹. As expected, the effect of the tight d functions is further reduced for the V{T,Q}Z basis set extrapolation (Table 3). In most cases, it amounts to less than 0.05 kcal mol⁻¹, with the main exceptions of -0.10 (HClO₄), -0.09 (ClO₃), and -0.06 (HOClO₂) kcal mol⁻¹.

3.4 Full-iterative connected triple excitations. Due to the steep computational cost of post-CCSD(T) valance calculations, using the regular VnZ basis sets (rather than the $V(n+d)Z$ basis sets) leads to significant computational savings. This approach is successfully used, for example, in W4lite, W4, and W4-F12 theories, which have been extensively applied to second-row molecules.^{16,19,25,27,37,48,54,55,56} We note that other composite ab initio theories, such as HEAT-345(Q),^{57,58,59,60,61} avoid this problem by using the aug-cc-pCV nZ basis sets in all-

electron calculations up to the CCSDT level, however, still use the cc-pVDZ basis set in the valence $\Delta(Q)$ calculations. Whereas a modified version of HEAT-345(Q) theory (mHEAT),⁵⁸ uses the cc-pVTZ and cc-pVDZ basis sets in the valence $\Delta T-(T)$ and $\Delta(Q)$ steps, respectively. Furthermore, post-CCSD(T) calculations are by necessity performed in conjunction with small basis sets (typically of double- ζ or triple- ζ quality). The results of the previous section demonstrate that the addition of tight d functions to the VDZ basis set can increase the $\Delta(T)$ component of the TAE by very significant amounts for chlorine oxides and molecules containing multiple second-row atoms. For example, in prominent cases, the $\Delta(T)$ component is increased by as much as 0.73 (S_4), 0.62 (C_2Cl_6), 0.49 (ClO_3), 0.48 ($HClO_4$), and 0.47 (S_3) kcal mol⁻¹. Thus, it is of interest to examine the effects of the tight d functions on the $\Delta T-(T)$ component of the TAE. Table 4 gives the differences between the $\Delta T-(T)$ component of the TAE calculated with the VnZ and $V(n+d)Z$ basis sets ($n = D-6$). We start by making two general observations regarding the effect of tight d functions on the $\Delta T-(T)$ component:

- With very few exceptions, the addition of tight d functions decreases the $\Delta T-(T)$ component.
- For all the hydrides, fluorides, and chlorine oxides, the tight d functions affect the $\Delta T-(T)$ component by very small amounts below 0.04 kcal mol⁻¹ (in absolute value). This is true even for systems containing highly polar bonds (e.g., AlF_3 and SiF_4) and/or pseudohypervalent systems (e.g., PF_5 , SF_6 , ClO_3 , and $HClO_4$).

Table 4. Differences between the $\Delta T-(T)$ component of the total atomization energy (TAE) obtained with VnZ and $V(n+d)Z$ basis sets ($TAE(VnZ)-TAE(V(n+d)Z)$ in kcal mol⁻¹) for a set of 45 second-row systems. Heatmapping is from red (largest positive values) to yellow (small values) to green (largest negative values).^a

		VDZ	VTZ	VQZ	V5Z	V6Z	V{D,T}Z	V{T,Q}Z
Hydrides	AlH	0.007	0.002	0.001	0.001	0.000	0.000	0.000
	AlH ₃	0.013	0.004	0.002	0.001	0.001	0.000	0.000
	SiH	0.005	0.003	0.001	0.000	0.000	0.002	0.000
	SiH ₄	0.018	0.009	0.004	0.001		0.005	0.000
	Si ₂ H ₆	0.027	0.013	0.004			0.007	-0.002
	PH ₃	0.006	0.005	0.001	0.000	0.000	0.005	-0.002
	HS	0.001	0.002	0.001	0.001	0.000	0.002	0.000
	H ₂ S	0.008	0.006	0.003	0.002	0.001	0.005	0.000
	HCl	0.008	0.008	0.004	0.002	0.001	0.007	0.001
Fluorides	AlF	0.008	0.004	0.002	0.001	0.000	0.002	0.000
	AlF ₃	0.005	0.004	0.002			0.004	0.000
	SiF	0.010	0.007	0.002	0.001	0.009	0.005	-0.001
	SiF ₄	0.012	0.012				0.012	
	PF ₃	0.009	0.013	0.004			0.014	-0.003
	PF ₅	0.009	0.016				0.019	
	SF ₆	0.005	0.021				0.028	
	ClF	0.000	0.004	0.001	0.001	0.000	0.006	-0.001
	ClF ₃	-0.011	0.004	0.000			0.011	-0.003
Oxides	ClF ₅	-0.026	0.004				0.016	
	SO	-0.010	-0.002	-0.002	0.000	0.000	0.001	-0.003
	SO ₂	0.006	0.017	0.008			0.022	0.002
	SO ₃	-0.001	0.021				0.031	
	HOCl	0.007	0.007	0.003	0.002		0.007	0.000
	HOClO	0.012	0.019	0.010			0.022	0.003
	HOClO ₂	0.016	0.031				0.037	
	HClO ₄	0.026	0.048				0.058	
	ClO	-0.003	0.002	0.000	0.002	0.000	0.004	-0.001
Pure second-row	OCIO	0.006	0.015	0.007			0.019	0.002
	ClO ₃	0.015	0.032				0.039	
	AlCl	0.018	0.014	0.007	0.005	0.002	0.012	0.002
	AlCl ₃	0.044	0.036	0.019			0.033	0.007
	P ₂	0.023	0.006	0.002	0.006	0.001	-0.001	-0.001
	P ₄	0.055	0.034	0.018			0.025	0.006
	S ₂	0.009	0.005	0.001	0.004	0.001	0.004	-0.003
	S ₃	0.061	0.044	0.024	0.018		0.037	0.009
	S ₄	0.115	0.084	0.047			0.071	0.020
Organic	Cl ₂	0.018	0.018	0.009	0.005	0.002	0.018	0.002
	CS	0.021	0.006	0.004	0.005	0.002	0.000	0.002
	CS ₂	0.027	0.017	0.011			0.013	0.006
	CF ₂ Cl ₂	0.019	0.018				0.018	
	CCl ₂	0.020	0.019	0.010	0.008		0.019	0.003
	CCl ₄	0.054	0.044				0.040	
	C ₂ Cl ₂	0.020	0.022	0.012			0.022	0.004
	C ₂ Cl ₄	0.056	0.047				0.044	
	C ₂ Cl ₆	0.093						
Overall stat. ^a	RMSD	0.031	0.024				0.023	
	MAD	0.021	0.017				0.017	
	MSD	0.019	0.017				0.017	

^aFootnotes *a* and *b* to Table 2 apply here.

For systems containing multiple second-row atoms, larger effects are observed. For C_2Cl_6 and S_4 , the $\Delta\text{T}-(\text{T})$ component of the TAE is affected by as much as 0.09 and 0.11 kcal mol⁻¹, respectively. Whereas for AlCl_3 , CCl_4 , C_2Cl_4 , S_3 , and P_4 the effect of the tight d functions ranges between 0.04–0.06 kcal mol⁻¹ (Table 4). Interestingly, the effect of the tight d functions on the $\Delta\text{T}-(\text{T})$ component diminishes only slightly when moving to the VTZ basis set. For example, it amounts to 0.03 (P_4), 0.04 (AlCl_3 , CCl_4 , and S_3), 0.05 (C_2Cl_4), and 0.08 (S_4) kcal mol⁻¹. For C_2Cl_6 , we were unable to obtain the $\Delta\text{T}-(\text{T})$ component in conjunction with the VTZ and V(T+d)Z basis sets, however, we expect that the effect of the tight d functions for C_2Cl_6 would be similar to that of S_4 .

Based on the above results, it is clear that in the context of high-level composite ab initio methods, tight d functions have to be included in the $\Delta\text{T}-(\text{T})$ calculations for problematic systems. For example, in W4 theory,²⁵ the $\Delta\text{T}-(\text{T})$ component is extrapolated from the V{D,T}Z basis set pair. For the above systems, we observe non-negligible effects for the $\Delta\text{T}-(\text{T})/\text{V}\{\text{D},\text{T}\}\text{Z}$ level of theory, namely, the inclusion of tight d functions reduces the $\Delta\text{T}-(\text{T})$ component by 0.02 (P_4), 0.03 (AlCl_3), 0.04 (CCl_4 , C_2Cl_4 , and S_3), and 0.07 (S_4) kcal mol⁻¹. Finally, we note that the effect of tight d functions is practically zero for all the molecules for which we were able to obtain results with the VQZ basis set (Table 4). Therefore, in theories such as W4.3 and W4.4, in which the $\Delta\text{T}-(\text{T})$ component is extrapolated from the V{T,Q}Z basis set pair, the extra d functions can be omitted.

3.5 Perturbative, noniterative connected quadruple excitations. Table 5 gives the differences between the $\Delta(\text{Q})$ component of the TAE calculated with the $\text{V}n\text{Z}$ and $\text{V}(n+d)\text{Z}$ basis sets ($n = \text{D}-6$). As is the case for the $\Delta\text{T}-(\text{T})$ component, the tight d functions have no visible effect on the $\Delta(\text{Q})$ component of the hydrides. However, their effect is not negligible for the fluorides. The addition of tight d functions to the VDZ basis set reduces the $\Delta(\text{Q})$

component by 0.02 (ClF₃ and PF₅), 0.05 (SF₆), and 0.08 (ClF₅) kcal mol⁻¹. Likewise, the sulfur and chlorine oxides are affected by similar amounts, most notably by 0.05 (HClO₄ and SO₂) and 0.06 (SO₃) kcal mol⁻¹.

Table 5. Differences between the $\Delta(Q)$ component of the total atomization energy (TAE) obtained with VnZ and $V(n+d)Z$ basis sets ($TAE(VnZ)-TAE(V(n+d)Z)$ in kcal mol⁻¹) for a set of 45 second-row systems. Heatmapping is from red (largest positive values) to yellow (small values) to green (largest negative values).^a

		VDZ	VTZ	VQZ	V5Z	V6Z	V{D,T}Z	V{T,Q}Z
Hydrides	AlH	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	AlH ₃	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	SiH	0.001	0.000	0.000	0.000	0.000	0.000	0.000
	SiH ₄	0.002	0.001	0.001	0.000		0.001	0.000
	Si ₂ H ₆	0.002	0.002	0.001			0.002	0.000
	PH ₃	0.003	0.002	0.001	0.000		0.001	0.000
	HS	0.000	-0.001	-0.001	0.000	0.000	-0.001	0.000
	H ₂ S	0.000	-0.001	-0.001	-0.001	0.000	-0.002	-0.001
	HCl	-0.001	-0.002	-0.002	-0.001	0.000	-0.003	-0.001
Fluorides	AlF	0.003	0.001	0.001	0.000	0.000	0.000	0.000
	AlF ₃	0.007	0.002	0.001			-0.001	0.000
	SiF	0.003	0.001	0.000	0.000	0.001	0.001	0.000
	SiF ₄	0.009	0.004				0.002	
	PF ₃	0.010	0.006				0.005	
	PF ₅	0.023						
	SF ₆	0.052						
	ClF	-0.001	-0.005	-0.003	-0.001	0.000	-0.006	-0.001
	ClF ₃	0.020	0.010				0.006	
ClF ₅	0.083							
Oxides	SO	0.004	0.001	0.001	-0.001	0.000	0.000	0.000
	SO ₂	0.047	0.030	0.018			0.023	0.009
	SO ₃	0.059	0.039				0.031	
	HOCl	-0.006	-0.007	-0.004	-0.002		-0.008	-0.002
	HOClO	-0.009	-0.006				-0.004	
	HOClO ₂	0.028	0.025				0.024	
	HClO ₄	0.054						
	ClO	-0.021	-0.019	-0.012	-0.004	-0.001	-0.018	-0.007
	ClO ₂	-0.005	0.002	0.002			0.005	0.002
ClO ₃	0.022	0.027				0.030		
Pure second-row	AlCl	-0.011	-0.007	-0.005	-0.001	-0.001	-0.006	-0.003
	AlCl ₃	-0.024	-0.020	-0.013			-0.018	-0.007
	P ₂	-0.015	-0.009	-0.005	-0.003	-0.001	-0.007	-0.002
	P ₄	-0.052	-0.029	-0.019			-0.019	-0.013
	S ₂	-0.015	-0.017	-0.011	-0.005	-0.002	-0.018	-0.006
	S ₃	-0.041	-0.031	-0.019	-0.008		-0.027	-0.009
	S ₄	-0.094	-0.060	-0.036			-0.046	-0.018
	Cl ₂	-0.011	-0.017	-0.011	-0.004	-0.001	-0.019	-0.006
Organic	CS	-0.024	-0.014	-0.008	-0.002	-0.001	-0.009	-0.003
	CS ₂	-0.057	-0.039	-0.023			-0.032	-0.011
	CF ₂ Cl ₂	-0.025	-0.019				-0.017	
	CCl ₂	-0.048	-0.033	-0.020	-0.006		-0.027	-0.011
	CCl ₄	-0.066	-0.046				-0.038	
	C ₂ Cl ₂	-0.034	-0.025	-0.015			-0.021	-0.007
	C ₂ Cl ₄	-0.077	-0.052				-0.042	
	C ₂ Cl ₆	-0.118						

For the systems with multiple second-row atoms, the effect of the tight d functions on the $\Delta(Q)$ component becomes more pronounced than for the fluoride and oxide systems. For the VDZ basis set, the inclusion of tight d functions increases the $\Delta(Q)$ component by as much as 0.05 (P_4 and CCl_2), 0.06 (CS_2), 0.07 (CCl_4), 0.08 (C_2Cl_4), 0.09 (S_4), and 0.12 (C_2Cl_6) kcal mol⁻¹. For the VTZ basis set, the effect is diminished but is still significant in the context of high-level composite ab initio methods such as W4 and W4. n theories, which achieve confident sub-kJ mol⁻¹ benchmark accuracy. For example, for the above systems, the inclusion of tight d functions increases the $\Delta(Q)$ component by 0.03 (P_4 and CCl_2), 0.04 (CS_2), 0.05 (CCl_4 and C_2Cl_4), and 0.06 (S_4) kcal mol⁻¹. For C_2Cl_6 , we were unable to obtain the $\Delta(Q)$ component in conjunction with the VTZ and V(T+d)Z basis sets, however, based on the above results, we expect that the effect of the tight d functions will approach the 0.1 kcal mol⁻¹ mark. For the V{D,T}Z basis set extrapolation, visible effects ranging between 0.03–0.05 kcal mol⁻¹ are found for systems such as SO_3 , ClO_3 , S_3 , S_4 , CS_2 , CCl_2 , CCl_4 , and C_2Cl_4 (Table 5).

We note that in W4lite and W4 theories, the $\Delta(Q)$ component is calculated in conjunction with the VDZ and VTZ basis sets, respectively. Therefore, our results indicate that tight d functions should be omitted with caution in high-level composite ab initio theories when treating fluorides, oxides, and systems containing multiple second-row atoms. Having said that, an inspection of Table 5 reveals that the inclusion of tight d functions tends to decrease the $\Delta(Q)$ component for the fluoride and oxide systems. In contrast, for the systems with multiple second-row atoms, the addition of tight d functions tends to systematically increase the $\Delta(Q)$ component. This is important since it means that the omission of tight d functions in post-CCSD(T) calculations results in error cancelation between the $\Delta T-(T)$ and $\Delta(Q)$ components for the systems with multiple second-row atoms, but for error reinforcement for the fluoride and oxide systems.

3.6 Post-CCSD(T) excitations as a whole. In the context of high-level composite ab initio methods, it is important to examine the effect of tight d functions on post-CCSD(T) contributions as a whole. Here, we will consider the following two variations, for which we have results for the entire set of molecules: T–(T)/VTZ + (Q)/VDZ and T–(T)/V{D,T}Z + (Q)/VDZ. We note that the latter level of theory is used for obtaining the post-CCSD(T) contributions in W4lite theory. Therefore, these results demonstrate the effect of including tight d functions in the post-CCSD(T) steps of a widely used composite ab initio method. W4lite theory approximates the valence CCSDT(Q)/CBS energy using the following basis set extrapolations: SCF/jul-cc-pV{5,6}Z + CCSD/jul-cc-pV{5,6}Z + (T)/jul-cc-pV{Q,5}Z + T–(T)/cc-pV{D,T}Z + (Q)/cc-pVDZ. Tight d functions are included in the SCF, CCSD, and (T) steps but not in the T–(T) and (Q) steps.²⁵ Table 6 shows the effects of including tight d functions in the latter two steps. Before examining these results, a comment is due on the accuracy of W4lite theory. For a set of 45 small molecules for which ATcT TAEs were available after W4lite theory was developed, W4lite theory attains an RMSD of 0.13 kcal mol⁻¹ and a MAD of 0.10 kcal mol⁻¹.¹⁶ Thus, in the following discussion effects of the tight d functions that are equal to or larger than 0.05 kcal mol⁻¹ will be deemed chemically significant within the accuracy of W4lite theory.

Table 6. Effect of tight d functions on post-CCSD(T) contributions as a whole to the TAEs of 45 second-row systems. The tabulated values are differences between the TAE component obtained with VnZ and $V(n+d)Z$ basis sets ($\text{TAE}(VnZ) - \text{TAE}(V(n+d)Z)$ in kcal mol^{-1}). Heatmapping is from red (largest positive values) to yellow (small values) to green (largest negative values).

		(Q)/VDZ T-(T)/VTZ	(Q)/VDZ T-(T)/V{D,T}Z
Hydrides	AlH	0.00	0.00
	AlH ₃	0.00	0.00
	SiH	0.00	0.00
	SiH ₄	0.01	0.01
	Si ₂ H ₆	0.01	0.01
	PH ₃	0.01	0.01
	HS	0.00	0.00
	H ₂ S	0.01	0.01
	HCl	0.01	0.01
Fluorides	AlF	0.01	0.01
	AlF ₃	0.01	0.01
	SiF	0.01	0.01
	SiF ₄	0.02	0.02
	PF ₃	0.02	0.02
	PF ₅	0.04	0.04
	SF ₆	0.07	0.08
	ClF	0.00	0.00
	ClF ₃	0.02	0.03
	ClF ₅	0.09	0.10
Oxides	SO	0.00	0.01
	SO ₂	0.06	0.07
	SO ₃	0.08	0.09
	HOCl	0.00	0.00
	HOClO	0.01	0.01
	HOClO ₂	0.06	0.07
	HOClO ₄	0.10	0.11
	ClO	-0.02	-0.02
	OCIO	0.01	0.01
	ClO ₃	0.05	0.06
Pure second-row	AlCl	0.00	0.00
	AlCl ₃	0.01	0.01
	P ₂	-0.01	-0.02
	P ₄	-0.02	-0.03
	S ₂	-0.01	-0.01
	S ₃	0.00	0.00
	S ₄	-0.01	-0.02
	Cl ₂	0.01	0.01
Organic	CS	-0.02	-0.02
	CS ₂	-0.04	-0.04
	CF ₂ Cl ₂	-0.01	-0.01
	CCl ₂	-0.03	-0.03
	CCl ₄	-0.02	-0.03
	C ₂ Cl ₂	-0.01	-0.01
	C ₂ Cl ₄	-0.03	-0.03

As expected, the post-CCSD(T) contributions for the hydrides in Table 6 are not affected by the inclusion of tight d functions. For pseudohypervalent fluorides (containing

more than four F atoms) are affected by appreciable amounts of 0.04 (PF₅), 0.08 (SF₆), and 0.10 (ClF₅) kcal mol⁻¹. Likewise, pseudohypervalent sulfur and chlorine oxides with multiple oxygen atoms are affected by appreciable amounts of 0.06 (ClO₃), 0.07 (HOClO₂ and SO₂), 0.09 (SO₃), and 0.11 (HClO₄) kcal mol⁻¹. As shown in the previous sections, the large effect on the post-CCSD(T) contribution is due to reinforcement of the effects on the T–(T) and (Q) components. Namely, in all cases, the addition of tight *d* functions reduces both the T–(T) and (Q) components. Overall, the effect of the tight *d* functions on the post-CCSD(T) contribution is clearly within the accuracy range of W4lite theory, and we recommend that tight *d* functions are included in the post-CCSD(T) calculations in second-row fluorides and oxides.

In contrast to the second-row fluorides and oxides, for the pure second-row systems (e.g., S₃ and S₄) and organic systems containing many second-row atoms (e.g., CCl₄ and C₂Cl₄), we obtain relatively small effects of the tight *d* functions on the post-CCSD(T) contributions. The largest effects are –0.03 (P₄, CCl₂, CCl₄, and C₂Cl₄) and –0.04 (CS₂) kcal mol⁻¹. As noted in the previous sections, for systems such as S₃, S₄, CCl₄, and C₂Cl₄, we obtain relatively large effects of the tight *d* functions on both the T–(T) and (Q) components. However, the relatively small overall effects on the post-CCSD(T) contribution as a whole is due to a systematic error cancelation between the T–(T) and (Q) components. For example, for S₄, the addition of tight *d* functions decreases the T–(T) component by 0.07 kcal mol⁻¹, but increases the (Q) component by 0.09 kcal mol⁻¹ (Tables 4 and 5). Another prominent example is C₂Cl₄, where the addition of tight *d* functions decreases the T–(T) component by 0.04 kcal mol⁻¹, but increases the (Q) component by 0.08 kcal mol⁻¹.

Due to the prohibitive computational cost of the post-CCSD(T) calculations, it would be desirable to have an *a priori* indicator for whether the addition of the tight *d* functions is likely to affect the post-CCSD(T) contribution to the TAEs by an appreciable amount. As

discussed above, this is particularly important for oxides and fluorides, for which the post-CCSD(T) contributions to the TAEs can exceed $0.05 \text{ kcal mol}^{-1}$. For example, 0.06 (ClO_3), 0.07 (HOClO_2 and SO_2), 0.08 (SF_6), 0.09 (SO_3), 0.10 (ClF_5), and 0.11 (HClO_4) kcal mol^{-1} . It has been previously shown that the addition of tight d functions can result in an appreciable increase in the overall $3d$ population on the second-row atom for systems such as HClO_4 .³⁶ Here, we will examine whether there is a correlation between the effect of the tight d functions on the wavefunction and on the post-CCSD(T) contributions. Table S1 of the Supporting Information lists the overall population of the $3d$ Rydberg orbitals on the second-row atoms taken from natural bond orbital (NBO) population analyses calculated at the HF/VDZ and HF/V(D+d)Z levels of theory. For the sake of simplicity, the overall population of the $3d$ orbitals on the second-row atoms is hereinafter denoted by $3d_{\text{pop}}$. Table S1 also lists the difference between the two populations ($\delta 3d_{\text{pop}}$) along with the effect of the extra d functions on the post-CCSD(T) contribution to the TAE (taken from the last column of Table 6). We note in passing that, as expected, $\delta 3d_{\text{pop}} > 0$ for all the systems, that is, the extra d functions increase the population of the $3d$ orbitals on the second-row atom. Further inspection of these results reveals that there is a reasonably high degree of correlation between $\delta 3d_{\text{pop}}$ and the post-CCSD(T) contribution to the TAEs. In particular, as illustrated in Figure 1a, we obtain squared correlation coefficients (R^2) of 0.891 for the subset of fluorides and 0.834 for the subsets of sulfur and chlorine oxides. We note that the squared correlation coefficient for the oxides increases to 0.897 if only the seven chlorine oxides are considered. A slightly better correlation is observed between the effect of the tight d functions on the post-CCSD(T) contribution to the TAE and the $3d_{\text{pop}}$ values, namely, we obtain $R^2 = 0.927$ (fluorides) and 0.868 (oxides) (Figure 1b).

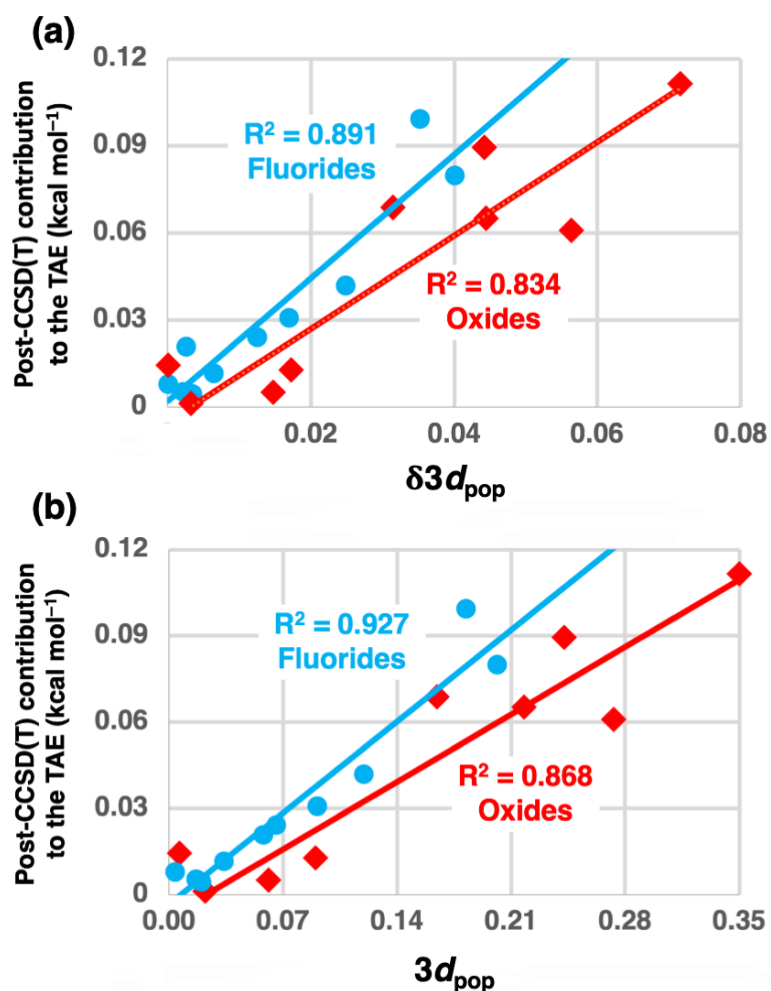


Figure 1. Correlation between the effect of the tight d functions on the overall post-CCSD(T) contribution to the TAE and (a) the effect of the tight d functions on the $3d$ population of the second-row atom ($\delta 3d_{\text{pop}}$) and (b) the overall population of the $3d$ orbitals of the second-row atom ($3d_{\text{pop}}$). The light blue circles correspond to the ten fluorides (AlF, SiF, ClF, AlF₃, PF₃, ClF₃, SiF₄, PF₅, ClF₅, and SF₆), and the red diamonds correspond to the ten oxides (SO, ClO, HOCl, SO₂, OClO, HOClO, SO₃, ClO₃, HOClO₂, and HClO₄) considered in the present work.

Although the correlations in Figure 1 are not perfect, these results suggest that the $\delta 3d_{\text{pop}}$ and $3d_{\text{pop}}$ values could serve as a useful *a priori* indicator for the effect of the tight d functions on the overall post-CCSD(T) contributions. For the systems considered here, we suggest that cut-off values of $\delta 3d_{\text{pop}} \geq 0.03$ or $3d_{\text{pop}} \geq 0.1$ indicate that the post-CCSD(T) contribution to the TAE might exceed $0.05 \text{ kcal mol}^{-1}$.

4. Conclusions

We examine the effect of the tight d functions in the cc-pV($n+d$)Z basis sets ($n = D, T, Q, 5, 6$) on post-SCF contributions to the total atomization energies (TAEs) for a diverse set of 45 second-row molecules with up to eight non-hydrogen atoms. The considered set includes nine hydrides (AlH, SiH, HS, HCl, H₂S, AlH₃, PH₃, SiH₄, and Si₂H₆), ten fluorides (AlF, SiF, ClF, AlF₃, PF₃, ClF₃, SiF₄, PF₅, ClF₅, and SF₆), ten oxides (SO, ClO, HOCl, SO₂, OClO, HOClO, SO₃, ClO₃, HOClO₂, and HClO₄), eight pure second-row systems (P₂, S₂, Cl₂, AlCl, S₃, AlCl₃, P₄, and S₄), and eight organic systems (CS, CS₂, CCl₂, CF₂Cl₂, CCl₄, C₂Cl₂, C₂Cl₄, and C₂Cl₆). This extensive set of molecules includes a diverse range of bonding situations and electronic structures and thus forms a good test set for evaluating the effect of tight d functions on post-SCF contributions to the TAEs. We consider contributions up to the CCSDT(Q) level, namely the Δ CCSD, Δ (T), Δ T–(T), and Δ (Q) correlation components. The effect of tight d functions on the Δ T–(T) and Δ (Q) contributions is particularly important in the context of post-CCSD(T) composite ab initio methods. Due to the daunting computational cost of valence post-CCSD(T) calculations, using the regular cc-pV n Z basis sets (rather than the cc-pV($n+d$)Z basis sets) is an effective strategy for reducing the computational cost. Our main conclusions can be summarized as follows:

- The effects of the tight d functions diminish with the highest angular momentum present in the basis set ($D \rightarrow T \rightarrow Q \rightarrow 5 \rightarrow 6$) and with the coupled cluster excitation level (Δ CCSD \rightarrow Δ (T) \rightarrow Δ T–(T) \rightarrow Δ (Q)).
- The Δ CCSD component of the TAE is strongly affected by the inclusion of tight d functions, in particular, with the VDZ, VTZ, and VQZ basis sets. For example, in conjunction with the VDZ basis set, the largest effects for each of the system types are +1.35 (hydrides, Si₂H₆), –0.64 (fluorides, SF₆), –2.19 (oxides, HClO₄), +1.72 (pure second-row, P₄), and +0.67 (organic, C₂Cl₆) kcal mol^{–1}. The effects are diminished for

the larger basis sets, however, even for the relatively large VQZ basis set, the following effects are observed +0.17 (hydrides, Si₂H₆), -0.43 (fluorides, SF₆), -0.95 (oxides, HClO₄), +0.12 (pure second-row, S₂ and P₄), and +0.23 (organic, C₂Cl₆) kcal mol⁻¹.

- With the exception of the hydrides, the $\Delta(T)$ component of the TAE is still affected by a considerable amount by the inclusion of tight *d* functions. The largest effects for each of the system types in conjunction with the VDZ basis set are -0.15 (fluorides, SF₆), -0.49 (oxides, ClO₃), -0.73 (pure second-row, S₄), and -0.62 (organic, C₂Cl₆) kcal mol⁻¹. The largest contributions in conjunction with the VTZ basis set are -0.28 (HClO₄), -0.25 (ClO₃), and -0.20 (S₄) kcal mol⁻¹. The largest contributions in conjunction with the VQZ basis set are -0.18 (HClO₄) and -0.16 (ClO₃) kcal mol⁻¹.
- Importantly, this work demonstrates, across a broad and diverse set of molecules, that tight *d* functions affect the post-CCSD(T) components of the TAEs by up to ~0.1 kcal mol⁻¹ even in challenging cases (e.g., SO₃, SF₆, S₄, HClO₄, ClF₅, and C₂Cl₆). Thus, in applications where this level of accuracy is not needed, tight *d* functions can be omitted in the valence post-CCSD(T) calculations.
- The $\Delta T-(T)$ component of the TAE is mainly affected in systems containing multiple second-row atoms. The systems that are affected by 0.05 kcal mol⁻¹ or more are +0.05 (P₄ and CCl₄), +0.06 (S₃ and C₂Cl₄), +0.09 (C₂Cl₆), and +0.11 (S₄). Moving to the larger VTZ basis set does not reduce these differences by a considerable amount.
- The effect of the tight *d* functions on the $\Delta(Q)$ component of the TAE is more pronounced than on the $\Delta T-(T)$ component. For about 25% of the systems, we obtain effects larger or equal to 0.05 kcal mol⁻¹ (in absolute value). Prominent examples include -0.05 (P₄ and CCl₂), -0.06 (CS₂), -0.07 (CCl₄), -0.08 (C₂Cl₄), -0.09 (S₄), -0.12 (C₂Cl₆), +0.05 (SO₂, HClO₄, and SF₆), +0.06 (SO₃), and +0.08 (ClF₅) kcal mol⁻¹.

- The $\Delta T-(T)$ component tends to be positive for most systems, and the $\Delta(Q)$ component tends to be positive for the oxides and fluorides but negative for the systems containing many second-row atoms. Thus, the omission of tight d functions in post-CCSD(T) calculations results in error cancelation between the $\Delta T-(T)$ and $\Delta(Q)$ components for the systems with multiple second-row atoms, but in error reinforcement for the fluoride and oxide systems. As a result, the effect of tight d functions on the overall post-CCSD(T) contributions for the fluoride and oxide systems is relatively large, for example, 0.06 (ClO_3), 0.07 (HOClO_2 and SO_2), 0.08 (SF_6), 0.09 (SO_3), 0.10 (ClF_5), and 0.11 (HClO_4) kcal mol^{-1} . These effects on the overall post-CCSD(T) contributions are thermochemically significant in the context of high-level composite ab initio methods such as W4 and W4lite theories.
- Finally, we find that for the 20 fluoride and oxide systems considered here, there are two *a priori* diagnostics that correlate well with the effect of the tight d functions on the overall post-CCSD(T) contributions. The two diagnostics are (i) the overall population of the $3d$ orbitals of the second-row atom ($3d_{\text{pop}}$) and (ii) the effect of the tight d functions on the population of the $3d$ orbitals ($\delta 3d_{\text{pop}}$). Either diagnostic could be used for assessing the potential effect of the tight d functions in post-CCSD(T) calculations.

SUPPLEMENTARY MATERIAL

NBO populations of 3*d* orbitals on the second-row atoms (Table S1), optimized geometries for all the structures (Table S2), and key absolute energies (Table S3).

ACKNOWLEDGMENTS

This research was undertaken with the assistance of resources from the National Computational Infrastructure (NCI), which is supported by the Australian Government. I gratefully acknowledge an Australian Research Council (ARC) Future Fellowship (FT170100373). I gratefully thank Professor Gershon (Jan M. L.) Martin (Weizmann Institute of Science) for fruitful discussions and insights on this topic.

REFERENCES

- ¹ Dunning, T. H. Gaussian Basis Sets for Use In Correlated Molecular Calculations. I. The Atoms Boron Through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007.
- ² Kendall, R. A.; Dunning, T. H.; Harrison, R. J. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.* **1992**, *96*, 6796.
- ³ Dunning, T. H.; Peterson, K. A.; Wilson, A. K. Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited. *J. Chem. Phys.* **2001**, *114* 9244.
- ⁴ Dunning Jr., T. H., Peterson, K. A.; and Woon, D. E. "Correlation consistent basis sets for molecular calculations", in Encyclopedia of Computational Chemistry (Eds.: P. v. R. Schleyer, N. L. Allinger, T. Clark), Wiley and Sons, Chichester, UK (1998).
- ⁵ Feller, D.; Peterson, K. A.; Hill, J. G. On the effectiveness of CCSD(T) complete basis set extrapolations for atomization energies. *J. Chem. Phys.* **2011**, *135*, 044102.

- ⁶ Feller, D. Benchmarks of improved complete basis set extrapolation schemes designed for standard CCSD(T) atomization energies. *J. Chem. Phys.* **2013**, *138*, 074103.
- ⁷ Martin, J. M. L. A simple ‘range extender’ for basis set extrapolation methods for MP2 and coupled cluster correlation energies. *AIP Conf. Proc.* **2018**, *2040*, 020008.
- ⁸ Karton, A. Effective basis set extrapolations for CCSDT, CCSDT(Q), and CCSDTQ correlation energies. *J. Chem. Phys.* **2020**, *153*, 024102.
- ⁹ Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. Basis-set convergence in correlated calculations on Ne, N₂, and H₂O. *Chem. Phys. Lett.* **1998**, *286*, 243.
- ¹⁰ Helgaker, T.; Klopper, W.; Bak, K. L.; Halkier, A.; Jørgensen, P.; Olsen, J. “Highly accurate ab initio computation of thermochemical data,” in *Quantum-Mechanical Prediction of Thermochemical Data, Understanding Chemical Reactivity*, edited by Cioslowski, J. (Kluwer, Dordrecht, 2001), Vol. 22, pp. 1–30.
- ¹¹ Martin, J. M. L.; Parthiban, S. “W1 and W2 theory and their variants: Thermochemistry in the kJ/mol accuracy range,” in *Quantum-mechanical Prediction of Thermochemical Data, Understanding Chemical Reactivity*, edited by Cioslowski, J. (Kluwer, Dordrecht, 2001), Vol. 22, pp. 31–65.
- ¹² Martin, J. M. L. Computational Thermochemistry: A Brief Overview of Quantum Mechanical Approaches. *Annu. Rep. Comput. Chem.* **2005**, *1*, 31.
- ¹³ Helgaker, T.; Klopper, W.; Tew, D. P. Quantitative quantum chemistry. *Mol. Phys.* **2008**, *106*, 2107.
- ¹⁴ Feller, D.; Peterson, K. A.; Dixon, D. A. A survey of factors contributing to accurate theoretical predictions of atomization energies and molecular structures. *J. Chem. Phys.* **2008**, *129*, 204105.

- ¹⁵ DeYonker, N.; Cundari, T. R.; Wilson, A. K. in *Advances in the Theory of Atomic and Molecular Systems, Progress in Theoretical Chemistry and Physics Vol. 19*, edited by Piecuch, P.; Maruani, J.; Delgado-Barrio, G.; Wilson, S. (Springer Netherlands, Dordrecht, 2009), pp. 197–224.
- ¹⁶ Karton, A.; Daon, S.; Martin, J. M. L. W4-11: A high-confidence dataset for computational thermochemistry derived from W4 ab initio data. *Chem. Phys. Lett.* **2011**, *510*, 165.
- ¹⁷ Peterson, K. A.; Feller, D.; Dixon, D. A. Chemical accuracy in ab initio thermochemistry and spectroscopy: current strategies and future challenges. *Theor. Chem. Acc.* **2012**, *131*, 1079.
- ¹⁸ Dixon, D. A.; Feller D.; Peterson K. A. A practical guide to reliable first principles computational thermochemistry predictions across the periodic table. *Annu. Rep. Comput. Chem.* **2012**, *8*, 1.
- ¹⁹ Karton, A. A computational chemist's guide to accurate thermochemistry for organic molecules. *WIREs Comput. Mol. Sci.* **2016**, *6*, 292.
- ²⁰ Feller, D.; Peterson K. A.; Dixon D. The Impact of Larger Basis Sets and Explicitly Correlated Coupled Cluster Theory on the Feller–Peterson–Dixon Composite Method. *Annu. Rep. Comput. Chem.* **2016**, *12*, 47.
- ²¹ Peterson, C.; Penchoff, D. A.; Wilson, A. K. Prediction of thermochemical properties across the periodic table: A review of the correlation consistent composite approach (ccCA) strategies and applications. *Annu. Rep. Comput. Chem.* **2016**, *12*, 3.
- ²² Karton, A. Quantum mechanical thermochemical predictions 100 years after the Schrodinger equation. *Annu. Rep. Comput. Chem.* **2022**, *18*, *in press*.
<https://doi.org/10.1016/bs.arcc.2022.09.003>
- ²³ Martin, J. M. L.; de Oliveira G. Towards standard methods for benchmark quality ab initio thermochemistry—W1 and W2 theory. *J. Chem. Phys.* **1999**, *111*, 1843.

- ²⁴ Boese, A. D.; Oren, M.; Atasoylu, O.; Martin, J. M. L.; Kallay, M.; Gauss, J. W3 theory: Robust computational thermochemistry in the kJ/mol accuracy range. *J. Chem. Phys.* **2004**, *120*, 4129.
- ²⁵ Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. W4 theory for computational thermochemistry: in pursuit of confident sub-kJ/mol predictions. *J. Chem. Phys.* **2006**, *125*, 144108.
- ²⁶ Karton, A.; Martin, J. M. L. Explicitly correlated W_n theory: W1-F12 and W2-F12. *J. Chem. Phys.* **2012**, *136*, 124114.
- ²⁷ Sylvetsky, N.; Peterson, K. A.; Karton, A.; Martin, J. M. L. Toward a W4-F12 approach: Can explicitly correlated and orbital-based ab initio CCSD(T) limits be reconciled? *J. Chem. Phys.* **2016**, *144*, 214101.
- ²⁸ Karton, A.; Taylor, P. R.; Martin, J. M. L. Basis set convergence of post-CCSD contributions to molecular atomization energies. *J. Chem. Phys.* **2007**, *127*, 064104.
- ²⁹ Karton, A. Post-CCSD(T) contributions to total atomization energies in multireference systems. *J. Chem. Phys.* **2018**, *149*, 034102.
- ³⁰ Bauschlicher Jr., C. W.; Partridge, H. The sensitivity of B3LYP atomization energies to the basis set and a comparison of basis set requirements for CCSD(T) and B3LYP. *Chem. Phys. Lett.* **1995**, *240*, 533.
- ³¹ Martin, J. M. L.; Uzan O. Basis set convergence in second-row compounds. The importance of core polarization functions. *Chem. Phys. Lett.* **1998**, *282*, 16.
- ³² Martin, J. M. L. Basis set convergence study of the atomization energy, geometry, and anharmonic force field of SO₂: The importance of inner polarization functions. *J. Chem. Phys.* **1998**, *108*, 2791.
- ³³ Bauschlicher Jr., C. W.; Ricca, A. Atomization Energies of SO and SO₂: Basis Set Extrapolation Revisited. *J. Phys. Chem. A* **1998**, *102*, 8044.

- ³⁴ Martin, J. M. L. Heat of atomization of sulfur trioxide, SO₃: a benchmark for computational thermochemistry. *Chem. Phys. Lett.* **1999**, *310*, 271.
- ³⁵ Martin, J. M. L. “Ab initio thermochemistry beyond chemical accuracy for first- and second-row compounds,” in *Energetics of Stable Molecules and Reactive Intermediates*, edited by M. E. Minas da Piedade, NATO ASI Series C 535 (Kluwer, Dordrecht, 1999), pp. 373–415.
- ³⁶ Martin, J. M. L. Heats of formation of perchloric acid, HClO₄, and perchloric anhydride, Cl₂O₇. Probing the limits of W1 and W2 theory. *J. Mol. Struct. (Theochem)* **2006**, *771*, 19.
- ³⁷ Karton, A.; Parthiban, S.; Martin, J. M. L. Post-CCSD(T) ab initio thermochemistry of halogen oxides and related hydrides XO_x, XOOX, HOX, XO_n, and HXO_n (X = F, Cl), and evaluation of DFT methods for these systems. *J. Phys. Chem. A* **2009**, *113*, 4802.
- ³⁸ Karton, A.; Tarnopolsky, A. Lamere, J.-F.; Schatz, G. C.; Martin, J. M. L. Highly Accurate First-Principles Benchmark Data Sets for the Parametrization and Validation of Density Functional and Other Approximate Methods. Derivation of a Robust, Generally Applicable, Double-Hybrid Functional for Thermochemistry and Thermochemical Kinetics. *J. Phys. Chem. A* **2008**, *112*, 12868.
- ³⁹ Feller, D.; Dixon, D. A. Extended benchmark studies of coupled cluster theory through triple excitations. *J. Chem. Phys.* **2001**, *115*, 3484.
- ⁴⁰ Wilson, A. K.; Dunning, T. H., Jr. SO₂ revisited: Impact of tight d augmented correlation consistent basis sets on structure and energetics. *J. Chem. Phys.* **2003**, *119*, 11712.
- ⁴¹ Wilson, A. K.; Dunning, T. H., Jr. The HSO–SOH Isomers Revisited: The Effect of Tight d Functions. *J. Phys. Chem. A* **2004**, *108*, 3129.
- ⁴² Feller, D.; Peterson, K. A.; Crawford, T. D. Sources of error in electronic structure calculations on small chemical systems. *J. Chem. Phys.* **2006**, *124*, 054107.

- ⁴³ Denis, P. A. Basis Set Requirements for Sulfur Compounds in Density Functional Theory: a Comparison between Correlation-Consistent, Polarized-Consistent, and Pople-Type Basis Sets. *J. Chem. Theory Comput.* **2005**, *1*, 900.
- ⁴⁴ Wang, N. X.; Wilson, A. K. Effects of Basis Set Choice upon the Atomization Energy of the Second-Row Compounds SO₂, CCl, and ClO₂ for B3LYP and B3PW91. *J. Phys. Chem. A* **2003**, *107*, 6720.
- ⁴⁵ Wang, N. X.; Wilson, A. K. Density Functional Theory and the Correlation Consistent Basis Sets: The Tight d Effect on HSO and HOS. *J. Phys. Chem. A* **2005**, *109*, 7187.
- ⁴⁶ Feller, D.; Dixon, D. A. Density Functional Theory and the Basis Set Truncation Problem with Correlation Consistent Basis Sets: Elephant in the Room or Mouse in the Closet? *J. Phys. Chem. A* **2018**, *122*, 2598.
- ⁴⁷ Papajak, E.; Truhlar, D. G. Convergent Partially Augmented Basis Sets for Post-Hartree–Fock Calculations of Molecular Properties and Reaction Barrier Heights. *J. Chem. Theory Comput.* **2011**, *7*, 10.
- ⁴⁸ Karton, A.; Sylvetsky, N.; Martin, J. M. L. W4-17: A diverse and high-confidence dataset of atomization energies for benchmarking high-level electronic structure methods. *J. Comput. Chem.* **2017**, *38*, 2063.
- ⁴⁹ Spackman, P. R.; Jayatilaka, D.; Karton, A. Basis Set Convergence of CCSD(T) Equilibrium Geometries Using a Large and Diverse Set of Molecular Structures. *J. Chem. Phys.* **2016**, *145*, 104101.
- ⁵⁰ Kállay, M.; Nagy, P. R.; Mester, D.; Rolik, Z.; Samu, G.; Csontos, J.; Csóka, J.; Szabó, P. B.; Gyevi-Nagy, L.; Hégyel, B.; *et al.* The MRCC Program System: Accurate Quantum Chemistry from Water to Proteins. *J. Chem. Phys.* **2020**, *152*, 074107.
- ⁵¹ Rolik, Z.; Szegedy, L.; Ladjanszki, I.; Ladoczki, B.; Kállay, M. An efficient linear-scaling CCSD(T) method based on local natural orbitals. *J. Chem. Phys.* **2013**, *139*, 094105.

- ⁵² Weinhold, F.; Landis, C. R.; Glendening, E. D. What is NBO analysis and how is it useful? *Mol. Phys.* **2016**, *35*, 399.
- ⁵³ Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; et al. Gaussian 16, rev. A.03; Gaussian, Inc.: Wallingford, CT, 2016.
- ⁵⁴ Karton, A.; Martin, J. M. L. Comment on “Revised electron affinity of SF₆ from kinetic data” [J. Chem. Phys. 136, 121102 2012)]. *J. Chem. Phys.* **2012**, *136*, 197101.
- ⁵⁵ Kroeger, A. A.; Karton, A. Thermochemistry of phosphorus sulfide cages: an extreme challenge for high-level ab initio methods. *Struct. Chem.* **2019**, *30*, 1665.
- ⁵⁶ Karton, A. High-level thermochemistry for the octasulfur ring: A converged coupled cluster perspective for a challenging second-row system. *Chem. Phys. Impact* **2021**, *3*, 100047.
- ⁵⁷ Thorpe, J. H.; Kilburn, J. L.; Feller, D.; Changala, P. B.; Bross, D. H.; Ruscic, B.; Stanton J. F. Elaborated thermochemical treatment of HF, CO, N₂, and H₂O: Insight into HEAT and its extensions. *J. Chem. Phys.* **2021**, *155*, 184109.
- ⁵⁸ Thorpe, J. H.; Lopez, C. A.; Nguyen, T. L.; Baraban, J. H.; Bross, D. H.; Ruscic, B.; Stanton J. F. High-accuracy extrapolated ab initio thermochemistry. IV. A modified recipe for computational efficiency. *J. Chem. Phys.* **2019**, *150*, 224102.
- ⁵⁹ Harding, M. E.; Vázquez, J.; Ruscic, B.; Wilson, A. K.; Gauss, J.; Stanton, J. F. High-accuracy extrapolated ab initio thermochemistry. III. Additional improvements and overview. *J. Chem. Phys.* **2008**, *128*, 114111.
- ⁶⁰ Bomble, Y. J.; Vázquez, J.; Kállay, M.; Michauk, C.; Szalay, P. G.; Császár, A. G.; Gauss, J.; Stanton, J. F. High-accuracy extrapolated ab initio thermochemistry. II. Minor improvements to the protocol and a vital simplification. *J. Chem. Phys.* **2006**, *125*, 064108.

⁶¹ Tajti, A.; Szalay, P. G.; Császár, A. G.; Kállay, M.; Gauss, J.; Valeev, E. F.; Flowers, B. A.; Vázquez, J; Stanton, J. F. HEAT: high accuracy extrapolated ab initio thermochemistry. *J. Chem. Phys.* **2004**, *121*, 11599.